MESOPOROUS ALUMINA MEMBRANE INCORPORATED CuO/CeO_2 CATALYST FOR OILY WASTEWATER TREATMENT

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Specials dedicated to my beloved mother and father, who taught me the best kind of knowledge to have is that which is learned for its own sake, for their encouragement and endless support

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ABSTRACT

Alumina hollow fibre exhibits an uncontrollable pore sieving which promotes intermediate pore blocking and fouling phenomenon during the operation, thus limits the membrane separation efficiencies. Therefore, to enhance filtration and selective properties of the membrane, mesoporous alumina was deposited on the outer surface of alumina hollow fibre using hydrothermal synthesis method in order to obtain a good crystalline membrane structure, highly uniform channel and narrow pore size distribution of membrane. The effect of different concentrations of mesoporous alumina suspension, synthesis times and calcination temperatures on the properties and separation performances of the prepared membranes were investigated. From the hydrothermal process, it was found that the optimum mesoporous alumina membrane was obtained at 1.2 M suspension concentration for 48 h reaction time, giving highest surface area of 236.495 m^2/g and 9.8 µm thickness of mesoporous alumina on top layer alumina hollow fibre. It can be said that the highest reactants concentration would increase the rate of mesoporous alumina membranes formation. In addition, mesoporous alumina membranes were further analyzed using different pollutants (PEG and BSA) by varying calcination temperature within range of 550–900 ºC for its selectivity performance. The highest PEG and BSA filtration were observed by mesoporous alumina membrane calcined at 800 ºC, with the percentage of rejection at 85.7 % and 53 %, respectively. This result leads for selecting the membrane for oily emulsion filtration at 1000 ppm. Since the membranes pose low flux at 14.28 $L/h.m^2$ with 52 % rejection on oily emulsion, modification on the membrane was carried out by incorporating the membranes with photocatalytic activity, at 3 wt. % of CuO/CeO_2 photocatalyst using sol gel Pechini. The highest oil flux and rejection at 1422 $L/h.m^2$ and 92 %, respectively, with the application of UV assisted online cleaning method. The results indicate that photocatalytic degradation of oil by CuO/CeO_2 photocatalyst improved the membrane separation performance. This study provides an insight on the improved performances of fabricated mesoporous alumina membrane incorporated CuO/CeO_2 photocatalyst on oily wastewater treatment which can be applied at industrial applications.

ABSTRAK

Gentian berongga alumina mempunyai liang pengayak yang tidak terkawal yang menggalakkan perantaraan penghalang liang dan fenomena kotoran tersumbat semasa rawatan air sisa, maka mengehadkan kecekapan pemisahan membran. Oleh itu, untuk meningkatkan penurasan dan sifat-sifat pemilihan membran, alumina mesoliang telah dimendakkan diatas permukaan luar gentian berongga alumina menggunakan kaedah sintesis hidroterma untuk mendapatkan struktur hablur membran yang baik, saluran yang sangat seragam dan membran taburan dengan saiz liang yang sempit. Kesan perbezaan kepekatan sebatian alumina mesoliang, masa sintesis dan suhu pengkalsian terhadap sifat-sifat dan prestasi pemisahan membran yang disediakan telah dikaji. Daripada proses hidroterma, optimum alumina mesoliang membran telah diperolehi pada 1.2 M kepekatan sebatian bagi 48 jam masa tindak balas, memberikan luas permukaan tertinggi iaitu 236.495 m^2/g dan 9.8 µm ketebalan alumina mesoliang di atas gentian berongga alumina. Boleh dikatakan bahawa kadar pembentukan membran alumina mesoliang akan meningkat dengan kepekatan bahan tindakbalas yang tinggi. Tambahan pula, membran alumina mesoliang boleh digunakan untuk analisis lanjutan menggunakan bahan cemar yang berbeza (PEG dan BSA) dengan membezakan suhu pengkalsinan dalam julat 550–900 ºC untuk prestasi kememilihan. Membran alumina mesoliang yang telah dikalsinkan pada suhu 800 ºC menunjukkan penurasan tertinggi terhadap PEG and BSA dengan peratusan penyingkiran masing masing pada 85.7 % dan 53 %. Keputusan ini menjurus kepada kememilihan membran untuk penurasan emulsi berminyak pada 1000 ppm. Disebabkan membran memiliki fluks rendah pada 14.28 $L/h.m^2$ dengan 52% penyingkiran pada emulsi berminyak, pengubahsuaian terhadap membran telah dijalankan dengan menggabungkan membran bersama aktiviti fotobermangkin, pada 3 % berat CuO/CeO_2 fotomangkin menggunakan *sol-gel Pechini*. Fluks minyak dan penolakan tertinggi masing-masing pada 1422 $L/h.m^2$ dan 92 % dengan aplikasi kaedah pembersihan atas talian berbantu UV. Keputusan ini menunjukkan perosotan fotobermangkin minyak oleh fotomangkin CuO/CeO_2 meningkatkan prestasi pemisahan membran. Kajian ini memberi gambaran pada penambahbaikan prestasi membran alumina mesoliang dengan fotomangkin CuO/CeO_2 direkabentuk dalam merawat air buangan berminyak yang boleh digunakan pada aplikasi perindustrian.

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LIST OF ABBREVIATIONS

$Al(NO_3)_3$	-	Aluminum Nitrate
Al_2O_3	-	Aluminum Oxide
AFM	-	Atomic Force Microscopy
BOD	-	Biodegradable Organic
BET	-	Brunauer, Emmett and Teller
BHJ	-	Bulk Heterojunction
CeO_2	-	Cerium oxide
COD	-	Chemical Oxygen Demand
CTAB	-	Cetyltrimethylammonium Bromide
CuO	-	Copper Oxide
FESEM	-	Field Emission Scannning Electron Microscope
H_2O	-	Water
HNO_3	-	Nitric Acid
MA	-	Mesoporous Alumina
MF	-	Microfiltration
MgO	-	Magnesium Oxide
NF	-	Nanofiltration
NMP	-	N-methyl-2-pyrrolidone
PAI	-	Polyamide-imide
PEG	-	Polyethylene Glycol
PEsf	-	Polythersulfone
PTFE	-	Polytetrafluoroethylene
PVA^-	-	Polyvinyl Alcohol
PVDF	-	Polyvinylideneflouride
RO	-	Reverse Osmosis

SEM	-	Scanning Electron Microscopy
SiO_2	-	Silica
TMP	-	Transmembrane pressure
UF	-	Ultrafiltration
UV	-	Ultra Violet light
UV-VIS	-	Ultra Violet- Visible Light
Wt %.	-	Weight percent
XRD	-	Xray Diffraction Analysis
ZnO	-	Zinc Oxide

LIST OF SYMBOLS

A	-	Effective membrane area, m^2
C_0	-	Initial concentration of pollutants
C_t	-	Final concentration of pollutants
C_f	-	Pollutants concentration in the feed, mol/L
C_p	-	Pollutants concentration in the permeate, mol/L
ΔP	-	Load Pressure, Pa
J	-	Pure water flux, $L/m^2.h$
l	-	Membrane thickness, m
Q	-	Permeate water volume over time, m^3/s
v	-	Permeate water volume, L
Δt	-	Time of the permeate collection, h
$\mathcal{E}$	-	Membrane porosity, %
P	-	Density of water, $0.998 g/cm^3$
S_{BET}	-	Specific surface area (m^2/g)
η	-	Water viscosity, 8.9×10^{-4} Pa.s
λ	-	Wavelength, cm
M	-	Molarity
ºC	-	Degree Celsius
µm	-	Micrometer
D_p	-	Pore Diameter

CHAPTER 1

INTRODUCTION

1.1 Research Background

Rapid development on petrochemical, palm oil, pharmaceutical and food industries have led to a large production of oily wastewater [1,2]. Direct discharge of this wastewater into water sources can cause a significant effect not only to the wildlife ecosystem but also to the human health [3-5]. In order to reduce the problem related to oil wastewater discharge, various conventional techniques have been invented and utilized. However, these conventional methods have several drawbacks such as high maintenance cost, require large space for installation and prone to generate toxic compounds during the treatment processes [5,6]. These drawbacks have resulted in renewed interest to use membrane technology in separating oil from wastewater. Membrane technology allows water that permeate through the membrane to be reused or discharged, with oil particles recovered at the retentate flow. This process is more effective and economical in treating oily wastewater.

Nowadays, membrane technology has become vital in a broad range of industrial applications. Membrane-based separation concepts were first introduced in biomedical laboratories and as analytical tools in chemistry which rapidly grows in production and commercial impact in the industries. Application of membrane technology can also be found in large-scale production of potable freshwater from sea for industrial applications. Furthermore, separation of gases and vapors in petrochemical processes also employs membrane technology in its operation. The implementation of membrane technology plays a prominent role in the removal of oil from oily wastewater. This is because it possesses a number of advantages such as lower energy requirements, more compact, can produce highly pure water permeates and fully automated treatment facilities [7]. The types of membrane can basically be classified into two categories, which are inorganic (ceramic) and organic membrane (polymeric). Ceramic membrane mostly consists of materials such as alumina, titania, zirconia oxides and silicon carbide. Meanwhile, polymer organic membrane that commonly used are polytetrafluoroethylene (Teflon PTFE), polyamide-imide (PAI) and polyvinylidene fluoride (PVDF).

Polymeric membranes have been extensively studied as the commercially utilized membrane in oily wastewater separation. There are two common types of membrane design which are flat sheet and hollow fibre. The capability of the polymer membrane to filter oily wastewater is depends on its features (morphology), materials used, preparation method and separation regime and process. Recently, ceramic membranes had grabbed some attention among the researchers because it possesses excellent membrane reliability and stability which contributes to high operation safety during oily wastewater treatment. Generally, ceramic membranes consist of symmetric and asymmetric structures. Commonly, the basis of asymmetric structures in ceramic membranes was due to the top layer framed by a coating method, which use the ceramic membrane as a support. The coating method enabled the support membrane to have a continuous layer which consists of a porous uniform sized layer [7-8]. Also, the layer acts as a selective layer which then helps to enhance the membrane performance via filtration and separation of oily wastewater.

Although ceramic membranes have been shown to enhance rejection and permeability, limited studies have focused on the sustainability of membrane performance during oily wastewater separation. Therefore, this study was performed to fill this gap by focusing on the development of photocatalytic mesoporous alumina membrane for the treatment of oily wastewater. Mesoporous alumina deposited on the outer surface of alumina hollow fibre was found capable to increase the rejection of oil particles. It was also found to operate as a high surface area for photocatalyst deposition

[8]. This hybrid membrane was extensively used with the purpose to limit the formation of cake (biofouling) on the surface and prolong the lifetime of the membrane [9,10]. Ceramic-based photocatalytic membranes were more preferred due to its excellent characteristic such as thermal, chemical and mechanical stability. Particularly, chemical stability of ceramic membrane can be determined from the resistance from the concomitant attack by hydroxyl radicals generated on the photocatalyst during the water filtration process under UV irradiation. This characteristic is important because it affect the stability and activity of photocatalyst, and integrity of substrate during deposition [10]. The membrane performance to remove oily wastewater was elucidated based on performance of photocatalytic membrane reactor under continuous feed flow and irradiation of ultraviolet (UV) light on the membrane surface. In this study, CuO/CeO_2 as catalyst was incorporated on the surface of mesoporous alumina membrane. The performance efficiency was determined by water permeation and percentage of oil rejection.

1.2 Problem Statement

Ceramic membrane is extensively studied due to its remarkable properties such as high chemical, thermal and mechanical stabilities and used widely as support. Nevertheless, ceramic membrane have some limitation, namely uncontrollable sieving in the treatment unit of oily wastewater. Moreover, it has wide pore size distributions and low surface area of separating layer [11]. Furthermore, unaltered pore size membrane commonly promotes secondary blocking and cake layer formation during the oil filtration [12]. This phenomenon may cause a failure in separation selectivity and permeability of oil molecule through the membrane pore. To enhance the properties of ceramic membrane, a thin layer of mesoporous material onto the surface of membrane was proposed. Mesoporous alumina is selected due to several advantages such as high hydrolytic stability and has different point of zero charge on the surface of membrane. In addition, mesoporous alumina has high surface area with a narrow pore size distribution and size small enough which can prevent the oil molecule penetration in such pores [12]. To enhance the performance of the membrane in oily wastewater separation, mesoporous alumina membrane was incorporated with a catalyst that can avoid fouling phenomenon and prolong the membrane lifetime [13].

1.3 Objectives of Study

The main objective of this study is to fabricate me m m m msoporous alumina membrane. Alumina hollow fiber membrane has been prepared using the phase inversion technique followed by a sintering phase. The thin layer of mesoporous alumina membrane is embedded onto the outer layer of alumina hollow fibre via hydrothermal method. The specific objectives in this study are:

1. To prepare mesoporous alumina membrane onto alumina hollow fibre using different concentrations and synthesis times

2. To characterize the properties of mesoporous alumina membrane before and after incorporation of CuO/CeO_2 catalyst

3. To investigate the performance of the catalyst incorporated mesoporous alumina membrane for oily wastewater treatment

1.4 Scope of Study

In order to achieve the objectives that were stated above, the scopes of study have been identified as

1. Preparing the mesoporous alumina membrane on alumina hollow fibre using hydrothermal synthesis.
    a. Varying the formulation preparation layer of mesoporous alumina membrane that used for coating on alumina support using different

concentration (0.6 M and 1.2 M) and synthesis times (24 h, 48 h and 72 h).

   b. Setting different calcination temperatures of mesoporous alumina membrane at 550 ºC, 700 ºC, 800 ºC and 900 ºC.

2. Characterizing mesoporous alumina membrane incorporated catalyst using various characterization techniques
   a. Performing the field emission scanning microscope (FESEM) for alumina support and thin layer mesoporous alumina prepared using different concentration (0.6 M and 1.2 M) and synthesis times (24 h, 48 h and 72 h).
   b. Performing x-ray diffraction (XRD) on mesoporous alumina membrane calcined at 550 ^{o}C, 700 ^{o}C, 800 ^{o}C and 900 ^{o}C.
   c. Performing surface area analysis (BET) on mesoporous alumina membrane prepared using different concentration (0.6 M and 1.2 M) with synthesis times (24 h, 48 h and 72 h)
   d. Investigating the performance of bare mesoporous alumina membrane based on percent rejection of polyethylene glycol (PEG) and bovine serum albumin (BSA) with molecular weights 10 kDa and 67 kDa, respectively.
3. Investigating the performance of mesoporous alumina membrane incorporated catalyst for oily wastewater treatment.
   a. Impregnating the 3 wt. % of CuO/CeO_2 catalyst using sol-gel method onto mesoporous alumina membrane
   b. Developing module for mesoporous alumina membrane incorporated catalyst to improve the performance of membrane
   c. Operating the calcination on mesoporous alumina membrane incorporated catalyst at 400 ºC and 500 ºC.
   d. Evaluating the performance of mesoporous alumina membrane for oily wastewater separation using different concentration ranging at 1000 ppm and 5000 ppm based on rejection percentage of oil and water permeation
   e. Operating the performance of mesoporous alumina membrane incorporated CuO/CeO_2 catalyst using three different methods of cleaning process for separation of oily wastewater (normal cleaning, UV assisted online cleaning and UV assisted on-off cleaning)

1.5 Significance of Study

The successful fabrication of macroporous and mesoporous alumina is applicable for simultaneous separation and reaction process. The porosity within bulk mesoporous alumina which also has the amount of accessible actives site can be used in oily separation. Therefore, a series of work have been conducted through coating of mesoporous alumina hollow fibre membrane with promising water permeability with high thermal stability. Membrane fouling becomes a main concern issues among the researcher, thus the development of photocatalytic mesoporous alumina membrane give beneficial effects such as shows the higher flux, cleaner permeate and membrane can be used for long time. Furthermore, implementation of this technology may produce the safe reusable water which helps to maintain the quality and relieve the unrelenting pressure on natural freshwater resources. To date, there is no study conducted on development of mesoporous alumina onto alumina support membrane incorporated with CuO/CeO_2 for oil removal. This study might be beneficial for removal of other macro and micro molecule and can be applied in palm oil refinery. Moreover, this type of membrane technology is promising to produce safe reusable water which helps to maintain the allowable quality of water to be discharged to natural freshwater resource.

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